

**Multilayer catalyst for autothermal steam reforming
of hydrocarbons and process for its use**

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Field of the Invention

5 The present invention relates to a multilayer catalyst for producing hydrogen by autothermal steam reforming.

Background of the Invention

10 For many commercial applications, it is desirable to be able to generate hydrogen from hydrocarbons. In order to achieve this goal, a number of methods have been developed.

15 According to one method, hydrocarbons, in the presence of water vapor and a suitable catalyst can be reacted at high temperatures to produce hydrogen, carbon monoxide and carbon dioxide. This reaction, which is referred to as "steam reforming" is strongly endothermic and, for example, may proceed according to the following reaction equation:



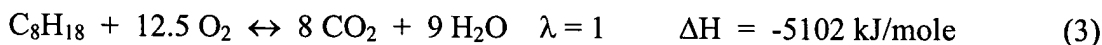
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The steam to carbon ratio, S/C in equation (1) is equal to 1.

25 Catalytic partial oxidation (abbreviated "CPO") is another well-known possibility for generating hydrogen. In that process, the hydrocarbons are reacted at a catalyst in the presence of oxygen to yield carbon monoxide and hydrogen according to the reaction equation for partial oxidation (2):



30 The air number λ is an important characteristic for the partial oxidation according to this process. It is defined as the ratio of the number of moles of oxygen used to the number of moles of oxygen needed for complete oxidation (see reaction equation (3)):



Complete conversion of the hydrocarbon to carbon monoxide and hydrogen according to
 5 Equation (3) requires an air number of $\lambda < 1$, ideally $\lambda = 4/12.5 = 0.32$.

Another possibility for obtaining hydrogen is “autothermal steam reforming.” This process combines steam reforming (equation (1)) with catalytic partial oxidation (equation (2)), such that the exothermic partial oxidation provides the heat of reaction
 10 required for the endothermic steam reforming. According to this process, the starting mixture can be preheated to a preheat temperature in order to allow the product mixture to be at thermodynamic equilibrium at the prevailing temperature at the reactor outlet. Autothermal steam reforming combines the advantages of catalytic partial oxidation (good start-up behavior) with those of steam reforming (high hydrogen yields). Thus, the
 15 process is well suited for on-board generation of hydrogen for mobile fuel cell systems, as well as for use in compact reformers for stationary fuel cell systems.

A number of variations of catalyst systems for autothermal reforming of hydrocarbons are known.

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For example, US 4,415,484 discloses a catalyst for use in an autothermal reforming reactor. This catalyst contains 0.01 to 6% rhodium, as well as 10 to 35% calcium oxide on an aluminum oxide support that also contains about 3 to 15% magnesium oxide. The catalyst is used in the form of pellets and is particularly
 25 distinguished by a low tendency to coking at low oxygen/hydrocarbon ratios. According to the ‘484 patent, a typical catalyst system for carrying out autothermal reforming contains an iron oxide catalyst for about a third of its length for the partial oxidation and a rhodium catalyst for two thirds of its length.

30 WO 98/55227 describes a bifunctional catalyst for the partial oxidation of hydrocarbons. The catalyst has both activity for dehydrogenation of hydrocarbons and

the ability to oxidize a hydrocarbon chain selectively. The dehydrogenating activity is provided by metals of Group 8 of the periodic system, while ionized oxygen carries out the selective oxidation. The sources of ionized oxygen are oxides crystallized in a fluorite or perovskite structure, such as zirconium oxide, cerium oxide, bismuth oxide,
5 *etc.* For example, one preferred catalyst is Pt/CeGdO, which is used in pellets with diameters of 1.125 to 1.5 inch (2.8 to 3.8 cm).

WO 98/48805 describes a process for catalytic production of hydrogen by a self-supporting partial oxidation and steam reforming of hydrocarbons in which a mixture of
10 the hydrocarbons and a gas containing oxygen and optionally steam is reacted over a catalyst that contains rhodium dispersed on a support that contains cerium and zirconium as cations. This catalyst is used in granulated form.

DE 197 27 841 A1 describes a process and a means for autothermal reforming of
15 hydrocarbons in which the fuel is passed through a feed device to a two-stage reformer reactor. The reformat produced is passed through a heat exchanger countercurrent to the starting materials for the reforming, so as to exchange heat. The fuel passed through the feed device, with the starting material, is brought directly to the reaction zone, which has a catalyst in which the combustion and reforming or catalysis is carried out. The
20 reformer reactor has a honeycomb structure coated with a catalyst in an upper region and a packing, coated with a catalyst in a lower region. A honeycomb structure can also be used instead of the packing.

EP 0 112 613 B1 describes a process for autothermal reforming of hydrocarbons
25 in which the partial oxidation occurs in one zone, and the steam reforming is spatially separated from it in a second zone. Catalysts containing Pt and Pd are used for the partial oxidation, and catalysts containing noble metals are used for the steam reforming.

WO 99/33567 describes catalysts for partial oxidation of hydrocarbons, the
30 monolithic supports of which have a multilayer structure with differing porosity. In this document, the multilayer structure refers to the supporting substrate.

A multilayer catalyst system for reforming methanol is described in DE 100 62 662 A1. This catalyst system contains a first catalytic component based on copper oxide and zinc oxide. At the lower layer, it catalyzes principally the steam reforming. There is
5 also a second, upper catalyst layer containing a noble metal (platinum or palladium) and a metal oxide, which primarily activates the partial oxidation of methanol. However, the catalyst system described here is not usable for autothermal reforming of hydrocarbons, because the base metal oxides (CuO, ZnO) are decomposed or reduced due to the higher temperatures, after which they alloy with the noble metal components. Consequently,
10 there is no long-term stability.

In EP 1 157 968 A1, a process is described for autothermal reforming of hydrocarbons. The process is operated adiabatically and requires a noble metal catalyst on a support.

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Unfortunately, the above-described technologies suffer from a number of disadvantages. For example, the processes described above have a high space requirement for reformer units, as well as a low hydrogen yield, which results in low reformer efficiency. Further, the lower reformer efficiency results in the complete fuel
20 cell power system (consisting of a fuel cell stack, reformer unit and control unit) having a lower overall efficiency that is only insignificantly better than those of modern optimized diesel systems for automobiles.

For reformers used in stationary fuel cell systems, the low efficiency results in a
25 lower total yield of electricity and heat. Consequently, the competitiveness with conventional combined heat and power systems (CHP systems) is reduced.

Thus, processes are needed for autothermal reforming of hydrocarbons with very high hydrogen yields so that they are highly suitable for use in mobile and stationary fuel
30 cell systems. Additionally, there is a need for suitable catalysts that can facilitate these processes.

Summary of the Invention

The present invention is directed to a catalyst and a process for autothermal catalytic steam reforming of hydrocarbons that uses the catalyst.

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According to one embodiment, the present invention provides a catalyst for autothermal catalytic reforming of hydrocarbons, said catalyst comprising:

- (a) a support; and
- (b) a multilayer catalyst substance, wherein said multilayer catalyst substance is applied to said support and said multilayer catalyst substance comprises:

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- (i) a lower catalyst layer, wherein said lower catalyst layer contacts said support and said lower catalyst layer is capable of preferentially catalyzing partial oxidation; and

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- (ii) an upper catalyst layer, wherein said upper catalyst layer is capable of preferentially catalyzing steam reforming.

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According to a second embodiment, the present invention provides a process for autothermal catalytic steam reforming of hydrocarbons. In this process, a starting mixture of hydrocarbons, oxygen and water or steam, heated to a preheat temperature, is passed over a catalyst made with multiple layers that can catalyze both partial oxidation and steam reforming of the hydrocarbons. The process may be used in reformer systems to generate hydrogen or hydrogen-containing fuel gases for fuel cells.

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According to a third embodiment, the present invention is directed to another process for autothermal catalytic steam reforming of hydrocarbons. This process is comprised of passing a starting mixture of hydrocarbons, oxygen and water or steam, heated to a preheat temperature, over a multilayer catalyst, wherein said process is operated adiabatically, and said multilayer catalyst is comprised of a support and a

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coating, wherein said coating is comprised of a multilayer catalyst substance in which a lower catalyst layer is capable of preferentially catalyzing partial oxidation and an upper catalyst layer is capable of preferentially catalyzing steam reforming.

5 **Brief Description of the Figure**

The preferred embodiments of the present invention have been chosen for purposes of illustration and description but are not intended to restrict the scope of the invention in any way. A preferred embodiment of certain aspects of the present invention is shown in the accompanying figure, wherein:

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Figure 1 is a representation of one possible structure of the catalyst of the present invention.

Detailed Description of the Invention

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The present invention will now be described in connection with preferred embodiments. These embodiments are presented in order to aid in an understanding of the present invention and are not intended, and should not be construed, to limit the invention in any way. All alternatives, modifications and equivalents that may become apparent to those of ordinary skill upon reading this disclosure are included within the spirit and scope of the present invention.

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This disclosure is not a primer on catalysts. Basic concepts known to those skilled in the art have not been set forth in detail.

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According to one embodiment, the catalyst of the present invention has, located on a support, a multilayer coating comprising at least two different layers. Preferably, each layer contains at least one platinum group metal on an oxide support material. The multilayer coating has not only a first, lower, catalyst layer that preferentially catalyzes the partial oxidation (CPO according to equation (2)) but also a second, upper, catalyst layer that exhibits activity primarily with respect to steam reforming (according to equation (1)). The lower layer is applied to a support, while the upper layer is applied to the lower layer. By contrast, in prior art technologies such as DE 100 62 662 A1, which uses different catalytic components, the layer sequence is reversed.

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In another embodiment, a process according to the present invention, a starting mixture of hydrocarbons, oxygen, and water or steam, preheated to a preheat temperature, is passed over a multilayer catalyst, with the reaction being carried out adiabatically. The process as a whole is considered a single step. That is, the product mixture is passed over a single multilayer catalyst that can provide the energy required for the endothermic steam reforming by the catalytic partial oxidation of the starting mixture. In this process, the temperature of the starting mixture rises from the preheat temperature to the required reaction temperature between 600 °C and 900 °C. Partial oxidation changes smoothly into steam reforming along the catalyst. The sequence of exothermic catalytic partial oxidation and endothermic steam reforming gives a uniform temperature profile in the catalyst, with no large temperature variations or peaks.

As noted above, the catalyst of the present invention has a catalyst substance on a support. The catalyst substance is applied to the geometric surfaces of the support in the form of a multiple layer coating. Preferred supports are monolithic honeycomb structures of ceramic or metal, open-cell ceramic or metallic foams, metal plates, or irregularly shaped parts. Preferably, the total thickness of the catalytic coating is between 20 and 200 µm.

In the case of a two-layer coating, the catalyst substance has a first, lower catalyst layer that preferentially catalyzes the partial oxidation, and a second, upper, catalyst layer that has preferential activity with respect to steam reforming. Figure 1 shows a schematic representation of one possible structure of the catalyst according to the present invention. As shown in the figure, the catalyst comprises a support (1) upon which a multilayer catalyst substance (2) is applied. That, in turn, is made up of a lower layer (3) and an upper layer (4). The lower catalyst layer can catalyze the partial oxidation and the upper catalyst layer can catalyze the steam reforming.

Each of the two different catalyst layers contains at least one platinum group metal on a finely divided oxide support. Therefore, these are “supported catalysts” in

which the noble metal is highly distributed (*i.e.*, a dispersion) on the oxide support material in the form of fine particles. In the context of this invention, the concept of “supported catalyst” refers only to the catalyst substance and must be distinguished from the catalyst, which is made up of the support (1) with the catalyst substance (2) applied to it.

The lower catalyst layer (3), which catalyzes the partial oxidation, contains as the noble metal preferably 0.1 to 5% by weight platinum, based on its total weight. Platinum has a high activity for oxidation of hydrocarbons. To adjust the oxidative activity to the requirements of the process, the catalyst substance can also contain other noble metals such as palladium or rhodium. It is preferable to use a catalyst substance that contains platinum on aluminum oxide and rare earth oxides.

The upper catalyst layer (4) (for steam reforming) preferably contains 0.1 to 5% by weight rhodium, based on its total weight, as the noble metal. Rhodium has high activity for steam reforming and at the same time a very low oxidation activity, compared with that of platinum. It is preferable to use a catalyst substance containing rhodium on an active aluminum oxide. This catalyst layer can also contain cerium oxide to reduce deposition of carbon and to increase its resistance to sulfur.

Examples of oxide supports for the platinum group metals include but are not limited to oxides such as aluminum oxide, silicon dioxide, titanium dioxide, or mixtures of them, and zeolites. It is preferred to use materials with specific surfaces greater than 10 m²/g in order to allow the highest possible dispersion of the catalytically active components on this large surface. The techniques for producing such a supported catalyst and for coating an inert support with it are known to persons skilled in the art.

The catalyst substance can also contain, for thermal stabilization, in addition at least one oxide selected from the group consisting of boron oxide, bismuth oxide, gallium oxide, oxides of the alkali metals, oxides of the alkaline earth metals, oxides of the subgroup elements and oxides of the rare earth metals. The additional oxides can be

present at, for example, concentrations of up to 40% by weight based on the total weight of the catalyst substance.

5 In one preferred embodiment, the lower catalyst layer and the upper catalyst layer each comprises a metal selected from the 8th subgroup elements of the periodic table and is located on an oxide support material. Preferably, the oxide support material is selected from the group consisting of aluminum oxide, silicon dioxide, titanium dioxide, boron oxide, bismuth oxide, gallium oxide, oxides of the alkali metals, oxides of the alkaline earth metals, oxides of the subgroup elements, rare earth oxides, mixtures of these oxides
10 and zeolites.

The multilayer catalyst according to the present invention has substantial advantages over conventional catalysts. For instance, the inventors have determined that, surprisingly application of the upper catalyst layer (for steam reforming) on the lower
15 layer that is active in oxidation, generally reduces the partial oxidation of the product mixture at the catalyst inlet. This avoids high temperature peaks that could destroy the catalyst. In addition, the yield of hydrogen is increased and the content of residual hydrocarbons, especially methane, is reduced. The process according to the present invention can be operated with aliphatic and/or aromatic hydrocarbons (methane,
20 propane, toluene, *etc.*) or hydrocarbon mixtures (*e.g.*, natural gas, gasoline, heating oil or diesel oil). Depending on the hydrocarbon used, one can operate at steam/carbon ratios, S/C, between 0.7 and 5. The air number of the starting mixture and its preheat temperature should be selected so that the temperature at the outlet from the catalyst has a temperature between 600 °C and 900 °C.

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The suggested process is only one part of a complete process to obtain hydrogen for mobile and stationary fuel cell units. The complete process includes, along with the autothermal reforming process, steps to remove carbon monoxide from the reformat, for instance, by one or more water gas shift steps. The reaction in the water gas shift steps is
30 exothermic and, in continuous operation of the reformer unit, can provide the quantity of heat needed to preheat the starting mixture to a suitable preheat temperature, such as

between about 270 °C and 350 °C. The starting mixture can also temporarily be preheated electrically for fast start-up of the reformer system. Because of the low thermal mass of the catalyst, full hydrogen production begins after only a few seconds.

5 Further embodiments of the present invention concern “graduated” or “three-layer” catalyst arrangements.

With graduated catalyst arrangements, the catalyst substance can be applied to a monolithic support with a length L that is penetrated from the inlet end to the outlet end
10 by flow channels, and can be made up of a lower catalyst layer lying directly on the support and an upper catalyst layer lying on the lower catalyst layer. In this case the lower layer is applied over the full length L of the support, and the upper layer is applied only to a certain segment, such as the exit part of the support. The precise form of the layer sequence depends on the structure, geometry, and operation of the reformer system.

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With three-layer catalyst arrangements the catalyst substance can have another catalyst layer, for the carbon monoxide conversion, for example. It is applied as a third layer to all or part of the second coating. The catalyst layer for the carbon monoxide conversion can contain, as the catalytically active components, at least one of the noble
20 metals Pt, Pd, Rh, Ru, Ir, Os and Au, on an oxide support material selected from the group consisting of aluminum oxide, silicon dioxide, titanium dioxide, rare earth oxides or mixtures of those oxides, and zeolites. This third catalyst layer may further comprise at least one rare earth metal and at least one base metal from the subgroup elements. Even more than three-layer structures, such as four-layer arrangements, are possible.

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The following example and the comparison example are intended to aid in explaining the essence of the invention in more detail. However, the invention is not limited by these examples.

EXAMPLES

Example 1

5 A two-layer catalyst was used to reform methane by a process according to the present invention. The catalyst was a catalytically coated ceramic honeycomb with a cell density of 62 cells/cm² and a volume of 30 ml.

The lower layer of the two-layer catalyst consisted of a platinum/aluminum oxide/cerium oxide/zirconium oxide supported catalyst. The upper layer of the catalyst
10 consisted of a rhodium/aluminum oxide supported catalyst. The total concentration of the catalytic coating was 150 grams/liter. The coating concentration of the noble metals was 0.5 g/liter platinum and 0.5 g/liter rhodium.

To carry out the autothermal reforming, the starting materials were heated to 600
15 °C and then passed together over the catalyst. The following flow rates of substances were used:

20 Methane:	152 g/h
Water:	454 g/h
Air:	319 std. liters/h

The inlet temperature of the mixture of substances was 610 °C, and the outlet temperature was 645 °C. The dry reformat from the two-layer catalyst contained 45.9% by volume hydrogen, compared with 43.4% by volume in the dry reformat from the
25 single-layer catalyst in Comparison Example 1. The CO content was only 4.1% by volume and the residual methane (CH₄) content could clearly be reduced to 1% by volume by use of the two-layer catalyst. **Table 1** summarizes the results.

Comparative Example 1

A catalytically coated ceramic honeycomb with a cell density of 62 cells/cm² and a volume of 30 ml was also used as the comparison example. The catalytic coating for the single-layer system consisted of a rhodium/aluminum oxide supported catalyst. It was applied to the honeycomb at a concentration of 150 grams per liter. The coating concentration of the rhodium was 1 g/liter. Methane was reformed by the process described in Example 1.

The starting materials were again heated to 600 °C, to carry out the autothermal reforming. Then they were passed jointly over the catalyst. The flow rates of methane, water and air were identical to those in Example 1.

The inlet temperature was 605 °C, and the outlet temperature was 640 °C. The dry reformat from the single-layer catalyst contained 43.4% by volume hydrogen (compared with 45.9% by volume for the two-layer catalyst according to the invention of Example 1). The concentrations of the undesired CO (4.8% by volume) and residual methane (1.7% by volume) were distinctly higher. The results are also presented in Table 1. From the results, one can see the superiority of the multilayer catalyst system according to the invention.

Table 1: Comparison of the multilayer catalyst according to the invention with a conventional single-layer catalyst for autothermal reforming of methane.

	Hydrogen (% by volume)	Carbon dioxide (% by volume)	Carbon monoxide (% by volume)	Residual methane (% by volume)
Example 1	45.9	13.8	4.1	1.0
Comparative Example 1	43.4	12.7	4.8	1.7